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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Liquid Adhesives

We, TOKYO SHIBAURA ELECTRIC COMPANY LIMITED, a corporation duly organised and existing under the law of Japan, and located at 72 Horikawa-cho, Kawasaki-shi, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with liquid adhesive compositions containing polyamide resin and epoxy resin.

It is known that polyamide resins act as curing agents for epoxy resins and in British Specification No. 1,013,898 it is shown that this curing effect is accelerated by the addition of a small amount of a phenolic resin to the mixture of polyamide and epoxy resins. The same specification describes and claims a process for the manufacture of an adhesive film which comprises applying a solution of epoxy resin onto a film of polyamide resin in the presence of a phenolic resin in either the polyamide resin or the epoxy resin, and drying. The film so formed is placed between the surfaces to be bonded and heat is applied to form the bond. Not only is curing rapid but the bond formed has improved adhesion and thermal resistance in comparison with a bond formed with a mixture of polyamide and epoxy resins alone.

In many cases, however, the use of a solid film-type adhesive is difficult or impossible and a liquid adhesive is more suitable. We have now developed a liquid adhesive composition in the form of a solution which cures rapidly by the concerted reaction mechanism between epoxy resins, polyamide resins and phenolic resins described in Specification No. 1,013,898.

[*Price 4s. 6d.*]

According to the present invention, therefore, we provide an adhesive composition comprising at least one polyamide copolymer resin, at least one epoxy resin and at least one phenol-formaldehyde resin and an organic solvent or mixture of organic solvents, said resins being dissolved in said solvent or solvent mixture.

Polyamide copolymers are well known in the art and are usually prepared by one of two methods. The first of these methods comprises copolymerising the monomers of two or more polyamide polymers to form a random copolymer; the second method comprises blending together two or more preformed polyamide polymers in the molten state to form a block copolymer. The polyamides formed by either of these methods are known as polyamide copolymers.

When the polyamide copolymer resin(s), the epoxy resin(s) and the phenol-formaldehyde resin(s) are dissolved together in a solvent, curing of course occurs rapidly and it is not therefore possible to store the adhesive composition of the invention in this form. Similarly, the epoxy resin and the polyamide copolymer resin cannot be stored dissolved together in the same solvent because curing again occurs, although less rapidly. The adhesive composition of the invention is therefore stored before use in two separate solutions, the first solution comprising the polyamide copolymer resin(s) in an organic solvent and the second solution comprising the epoxy resin(s) in an organic solvent; at least one of said solutions contains the phenol formaldehyde resin(s).

The two solutions are put on the market together and the user first mixes together enough of the two solutions to give the

amount of adhesive he requires; he then applies the resulting adhesive composition to at least one of the surfaces to be bonded, generally lets the solution dry until it becomes tacky and finally presses the two surfaces together and cures the composition at an elevated temperature to form the bond.

Any epoxy resin which is soluble in a suitable organic solvent can be used in the adhesive compositions of the invention but it is preferred to use those having an epoxy equivalent of from 500 to 1025. Similarly, it is preferred to use phenol-formaldehyde resins of the novolak or resole type.

Polyamide copolymers suitable for use in the adhesive compositions of the invention are derived from two or more polyamides or the monomers thereof, as described hereinabove. Suitable polyamides include 6-nylon, 6.6-nylon, 6.10-nylon and 10.10 nylon, a copolymer of 6-nylon, 6.6-nylon and 6.10-nylon being particularly preferred (a copolymer of this type is produced by E. I. du Pont de Nemours and Company under the Trade Mark "Zytel 39").

In the two-component storage stable composition, the solvent for the polyamide copolymer solution is preferrably methanol or ethanol and the solvent for the epoxy resin solution is preferably acetone or tetrahydrofuran.

The weight ratio of polyamide copolymer resin, epoxy resin and phenol formaldehyde resin in the adhesive composition is preferably 100:5 to 30:10 to 70 respectively.

In order that the invention may be more fully understood, the following Examples, in which all parts and percentages are by weight, are given by way of illustration only.

Example 1.

Solution A, a 20% solution of a mixture containing an equal weight of a novolak type phenolic resin and an epoxy resin having an epoxy equivalent of from 875 to 1025 in acetone was prepared.

Solution B containing 15 parts of a copolymer of 6-nylon, 6.6-nylon and 6.10-nylon dissolved in 85 parts of methanol was prepared.

Three parts of Solution A and four parts of Solution B were mixed slowly and with stirring to form a uniform mixture. The resultant mixture was applied to a polished steel plate in an amount of about 200 g per m^2, and then dried until tacky. Another polished steel plate to be bonded was then placed on the adhesive layer on said first plate and, after curing for 15 minutes at 150°C with the plates subjected to a pressure of about 5 Kg/cm^2, excellent adhesion was obtained.

By using the adhesive of this invention, it is possible to lower the curing temperature and to shorten the curing time remarakably as compared with the case of using a conventional epoxy-polyamide type adhesive in which one hour and a temperature of 175°C may be required for curing.

Thus resultant bond part did not soften on heating even up to a temperature of 200°C but if this bond is heated over 300°C, the bonded article can be stripped off easily. In the case of a conventional polyamide type adhesive, the temperature of stripping is about 200°C.

The tensile shear strength of the above article bonded by the adhesive composition of the invention was about 350 kg/cm^2, while in the case of a conventional epoxy-polyamide type adhesive this strength may be about 300 kg/cm^2.

Example 2.

188 g of phenol and 150 g of 40% formalin were added to a three neck distillation flask equipped with a reflux condenser, a thermometer and a stirrer and 3 cc of 0.5 N HCl aqueous solution was added as a catalyst. The contents of the flask were then heated on a water bath at a temperature of about 100°C to effect the condensation reaction. After the solution became cloudy, 340 g of 15% aqueous solution of NaOH was poured in, and 186 g of epichlorhydrin were slowly added to the solution over about 30 minutes at a reaction temperature of 65°C while stirring. After the reaction had continued for 2 hours, a viscous and yellowish brown liquor precipitated in the bottom of the flask, and was taken out from the flask and washed with distilled water several times to remove NaCl produced simultaneously. The viscous liquor was then dissolved in acetone and was filtered and the resultant filtrate was heated gently to remove the solvent, that is acetone, by evaporation. A mixed solid resin comprising novolak type phenolic resin and epoxy resin was thus formed by epoxidation of the phenolic resin.

Solution A, a 20% solution of said solid resin dissolved in tetrahydrofuran was prepared.

Solution B containing 15 parts of a polyamide copolymer as used in Example 1 dissolved in 85 parts of methanol was prepared.

Three parts of solution A and four parts of solution B were mixed as in Example 1 to prepare a viscous adhesive. The same adhesion test as in Example 1 was carried out using the prepared viscous adhesive, and the results were similar to those in Example 1.

Example 3

10 cc of 0.5 N NaOH aqueous solution was used as the catalyst in place of 3 cc of 0.5 N HCl used in Example 2, and the same procedures were repeated as in Example 2 to obtain a resole type phenolic resin. This phenolic resin was partially epoxidised to pre-

pare a mixture of resole type phenolic resin and epoxy resin, and this mixture was dissolved in tetrahydrofuran at a concentration of 20% to make Solution A.

Solution B was prepared as in Example 2.

Three parts of solution A and four parts of solution B were mixed as in Example 1 to prepare a viscous adhesive.

The same adhesion test as in Example 1 was carried out with this adhesive and the results were similar to those in Example 1.

EXAMPLE 4

Solution A, a 20% solution of epoxy resin having an epoxy equivalent of about 500 in tetrahydrofuran as a solvent was prepared.

Solution B, containing 13.5 parts of a polyamide copolymer as used in Example 1 and 1.5 parts of a resole type phenolic resin dissolved in 85 parts of methanol was prepared.

Both Solutions A and B were used as in Example 1, and similar results were obtained.

EXAMPLE 5

Solution A, a 20% mixed solution of 10 parts of epoxy resin having an epoxy equivalent of about 500 and 1 part of resole type phenolic resin in a solvent of tetrahydrofuran was prepared.

Solution B a 15% mixed solution of 10 parts of a polyamide copolymer as used in Example 1 and 1 part of resole type phenolic resin in methanol was prepared.

One part of Solution A and two parts of Solution B were mixed, the mixture was used as in Example 1, and similar results were obtained.

In the Examples, the weight ratios of polyamide copolymer to epoxy resin to phenol-formaldehyde resin in the adhesive compositions were as follows:—

Example 1:	100:	50:	50
Example 2:	100:	130:	70
Example 3:	100:	130:	70
Example 4:	100:	110:	10
Example 5:	100:	50:	15

WHAT WE CLAIM IS:—

1. An adhesive composition comprising at least one polyamide copolymer resin, at least one epoxy resin and at least one phenol-formaldehyde resin and an organic solvent or mixture of organic solvents, said resins being dissolved in said solvent or solvent mixture.

2. A composition according to claim 1 in which the epoxy resin has an epoxy equivalent of from 500 to 1025.

3. A composition according to claim 1 or 2, in which the polyamide copolymer is a copolymer of two or more of 6-nylon, 6.6-nylon, 6.10-nylon and 10.10-nylon.

4. A composition according to claim 3 in which the polyamide copolymer is a copolymer of 6-nylon, 6.6-nylon and 6.10-nylon.

5. A composition according to any of claims 1 to 4, in which the solvent mixture comprises methanol or ethanol and acetone or tetrahydrofuran.

6. A composition according to any of claims 1 to 4, in which the weight ratio of polyamide copolymer resin, epoxy resin and phenol formaldehyde resin is, respectively, 100: 50 to 130: 10 to 70.

7. A method of bonding using an adhesive composition as claimed in any of claims 1 to 6, which comprises mixing together two separate solutions, a first solution comprising the polyamide copolymer resin(s) in an organic solvent and a second solution comprising the epoxy resin(s) in an organic solvent, at least one of said solutions containing the phenol-formaldehyde resin(s), applying the resulting adhesive composition to at least one of the surfaces to be bonded and curing the composition at an elevated temperature to form the bond.

8. An adhesive composition according to claim 1 substantially as herein described in any of the Examples.

9. A method of bonding according to claim 7 substantially as hereindescribed in any of the Examples.

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